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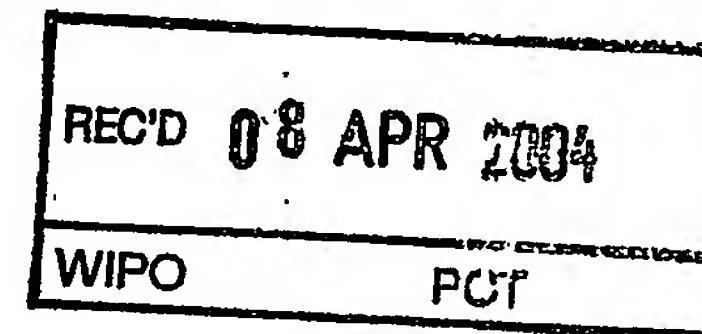
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REPUBLIC OF SOUTH AFRICA

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INDUSTRY

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the documents attached hereto are true copies of the Forms P2, P6,  
provisional specification and drawings of South African Patent Application  
No. 2003/6523 in the name of Sasol Technology (Proprietary) Limited

Filed : 21 August 2003  
Entitled : Extraction of Oxygenates from  
a Hydrocarbon Stream

Geteken te in die Republiek van Suid-Afrika, hierdie  
Signed at PRETORIA in the Republic of South Africa, this 16<sup>th</sup> dag van March 2004  
dag van March 2004  
day of

A handwritten signature in cursive script, appearing to read "P. Goepa".  
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FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)					
71	SASOL TECHNOLOGY (PROPRIETARY) LIMITED				
APPLICANTS SUBSTITUTED:					DATE REGISTERED
71					
ASSIGNEE(S)					DATE REGISTERED
71					
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54	EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM				
ADDRESS OF APPLICANT(S)/PATENTEE(S)					
1 STURDEE AVENUE, ROSEBANK, 2196, GAUTENG, SOUTH AFRICA					
ADDRESS FOR SERVICE				S & F REF	
74	SPOOR & FISHER, SANDTON			PA135755/P	
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## APPLICATION FOR A PATENT

AND ACKNOWLEDGEMENT OF RECEIPT 21.08.03  
(Section 30 (1) – Regulation 22)

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The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

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REPUBLIC OF SOUTH AFRICA  
S & F PREFERENCE

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FULL NAME(S) OF APPLICANT(S)

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TITLE OF INVENTION

54 EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. THE EARLIEST PRIORITY CLAIM IS:

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THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.

21 01

THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND IS BASED ON APPLICATION NO.

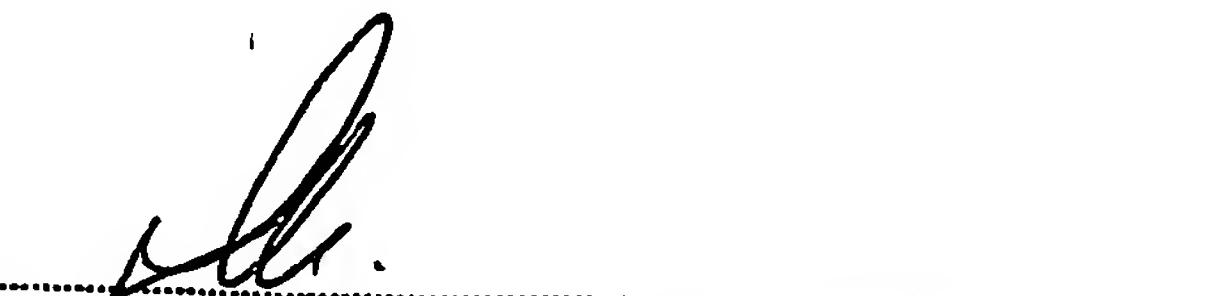
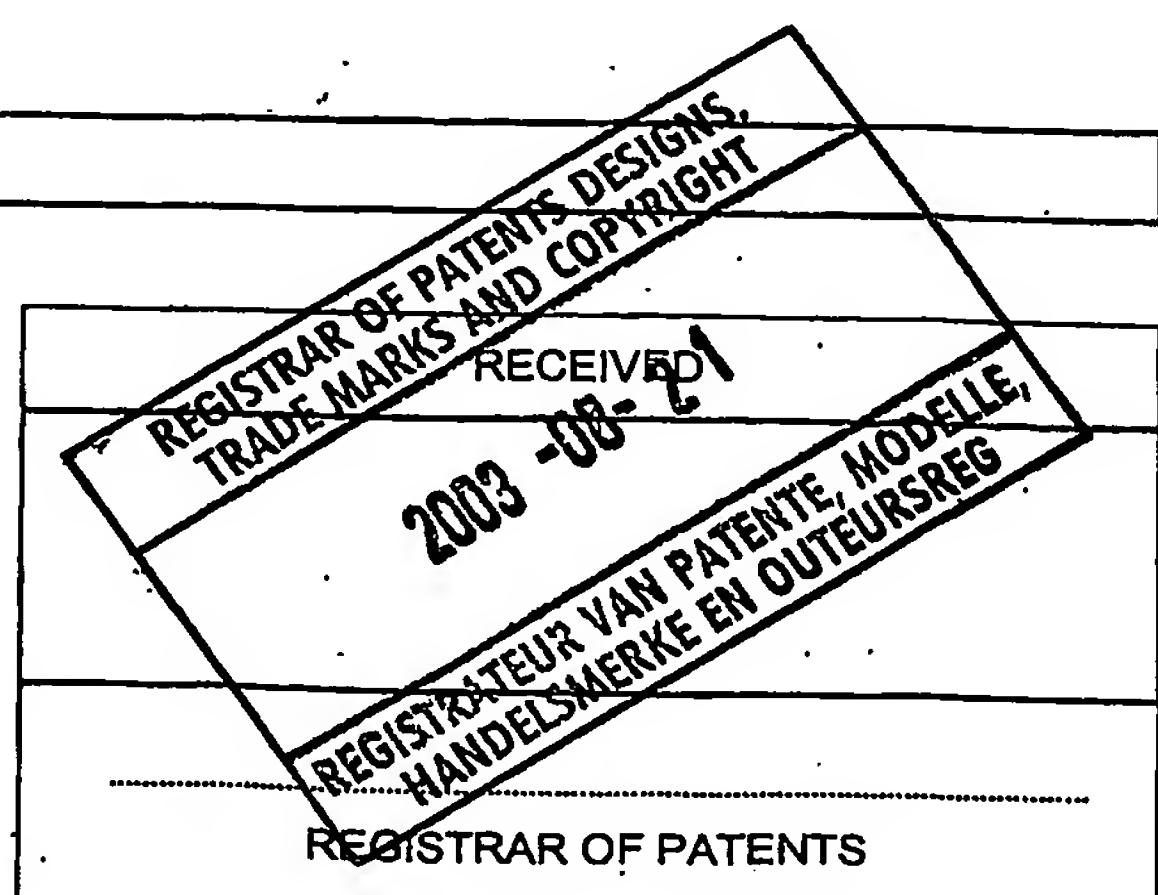
21 01

THIS APPLICATION IS ACCCOMPANIED BY:

- 1. A single copy of a provisional specification of 13 pages.
- 2. Drawings of sheets
- 3. Publication particulars and abstract (Form P.8 in duplicate).
- 4. A copy of Figure of the drawings (if any) for the abstract.
- 5. Assignment of invention.
- 6. Certified priority document.
- 7. Translation of the priority document.
- 8. Assignment of priority rights.
- 9. A copy of the Form P.2 and the specification of S.A. Patent Application No .
- 10. Declaration and power of attorney on Form P.3.
- 11. Request for ante-dating on Form P.4.
- 12. Request for classification on Form P.9.
- 13. Form P.2 in duplicate.
- 14. Other.

74 ADDRESS FOR SERVICE: SPOOR &amp; FISHER, SANDTON

Dated: 21 August 2003


SPOOR & FISHER  
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REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

## PROVISIONAL SPECIFICATION

(Section 30(1) – Regulation 27)

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FULL NAMES OF APPLICANTS

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TITLE OF INVENTION

54 EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM

## **EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM**

### **BACKGROUND OF THE INVENTION**

This invention relates to a method for extracting oxygenates from a hydrocarbon stream.

Many methods for extracting oxygenates from hydrocarbon streams are known. Such extraction methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction.

This invention relates to a process for extracting or separating oxygenates from the condensation product of a low temperature Fischer-Tropsch reaction, to produce a condensation product that is particularly suitable for the production of linear alkyl benzene.

### **SUMMARY OF THE INVENTION**

According to the invention there is provided a method for extracting oxygenates from the condensation product of a low temperature Fischer-Tropsch reaction, while preserving the olefin content of the condensation product. The condensation product typically contains 15% to 30% by weight olefins, usually 15% to 25% by weight olefins, 60% to 80% by weight paraffins and 5% to 10% by weight oxygenates.

The oxygenate extraction process is a liquid-liquid extraction process that preferably takes place in an extraction column using a polar organic solvent, preferably methanol, and water as the solvent, wherein the polar organic solvent and water are added separately to the extraction column.

The hydrocarbon stream is fed into the extraction column at, or near, the bottom thereof, a polar organic solvent stream is fed into the extraction column at, or near, the top thereof, and a water stream is fed into the extraction column between the hydrocarbon stream and polar organic solvent stream.

An extract from the liquid-liquid extraction may be sent to a solvent recovery column from which a tops product comprising polar organic solvent, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins. A bottoms product from solvent recovery column may also be recycled to the extraction column.

A raffinate stream from the extraction column is preferably sent to a stripper column from which a hydrocarbon stream containing more than 90% by weight olefins and paraffins and typically less than 0.2% by weight, preferably less than 0.02% by weight, most preferably less than 0.01% by weight oxygenates exits as a bottoms product.

The solvent preferably has a water content of more than 3% by weight, more preferably a water content of about 5% - 15% by weight.

#### BRIEF DESCRIPTION OF THE DRAWING

The Figure is a block diagram of a process of the Invention for extracting oxygenates from a hydrocarbon stream.

### DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to a process for extracting oxygenates from a hydrocarbon condensate stream from a low temperature Fischer-Tropsch reaction. The substantially oxygenate-free hydrocarbon stream can be used in the production of linear alkyl benzene.

In the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen) obtained either from the gasification of coal or the reforming of natural gas, is reacted over a Fischer Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates.

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C, preferably 210°C - 260°C, and a pressure in the range of 18-50 bar (gauge), preferably between 20-30 bar (gauge), in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the major product of the reaction and may, for example, be hydrocracked to produce diesel and naphtha.

The lighter hydrocarbon vapour phase which comprises gaseous hydrocarbon products, unreacted synthesis gas and water is condensed to provide a "condensation product" which comprises an aqueous phase and a hydrocarbon condensation product phase.

The hydrocarbon condensation product includes olefins, paraffins in the C<sub>4</sub> to C<sub>26</sub> range, and oxygenates including alcohols, esters, aldehydes, ketones and acids.

Typically, a hydrocarbon condensation product for a low temperature Fischer-Tropsch reaction contains 15%-30% by weight olefins, 60%-80% by weight paraffins, and 5%-10% by weight oxygenates. It has, surprisingly, been found that even though this condensation product has a low olefin content, it can be used in the production of linear alkyl benzene. However, it is necessary to first extract the oxygenates as these species have a negative effect on the alkylation reaction. There is therefore a need to find a process for extracting oxygenates, but at the same time preserve the olefin concentration. For the production of linear alkyl benzene, the hydrocarbon condensate product is fractionated into a C<sub>10</sub> - C<sub>13</sub> cut which, by way of example, contains 25% by weight olefins, 68% by weight paraffins and 7% by weight oxygenates.

In the prior art, many methods of extracting oxygenates from hydrocarbon streams are suggested. Such removal methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction. It has been found that liquid-liquid extraction is a preferred method of oxygenate extraction because, if the correct solvent is selected, the olefin concentration can be preserved. In liquid-liquid extraction, the solvent can be any polar material that has partial miscibility with the feed stream 14, such as tri-ethanol amine, tri-ethylene glycol with between zero and 20% water, acetonitrile with between 5% and 20% water, acetol, diols, methanol, or ethanol and water.

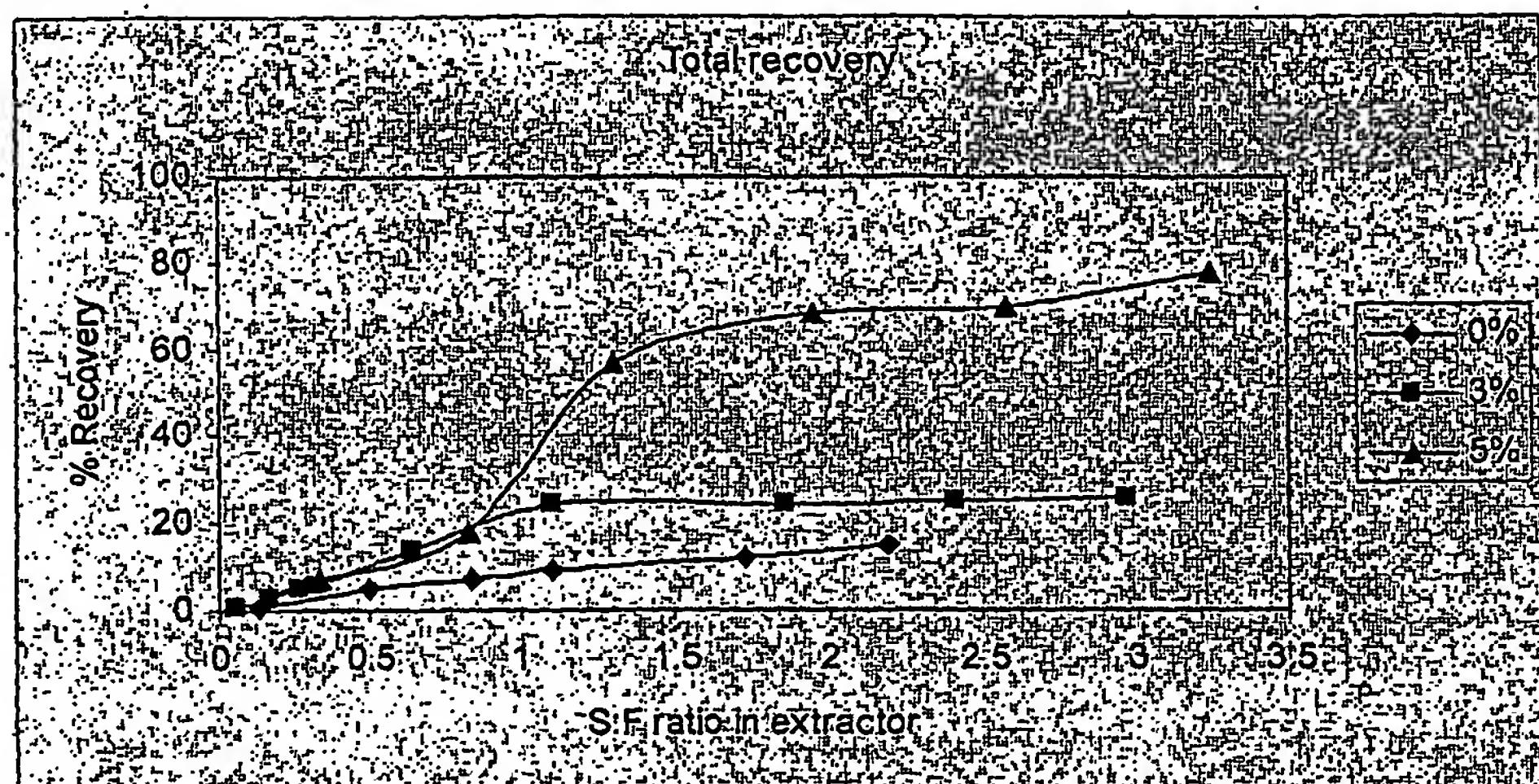
According to the invention, a preferred solvent in a liquid-liquid extraction column is a polar organic solvent, in this case methanol, and water. Usually, this type of solvent would be added as a mixture at the top of the liquid-liquid extraction column. It has been found that it is possible to obtain a higher recovery of olefins and paraffins, with a lower oxygenate content

(i.e. a purer product) by adding the polar organic solvent and the water separately to the liquid-liquid extraction column.

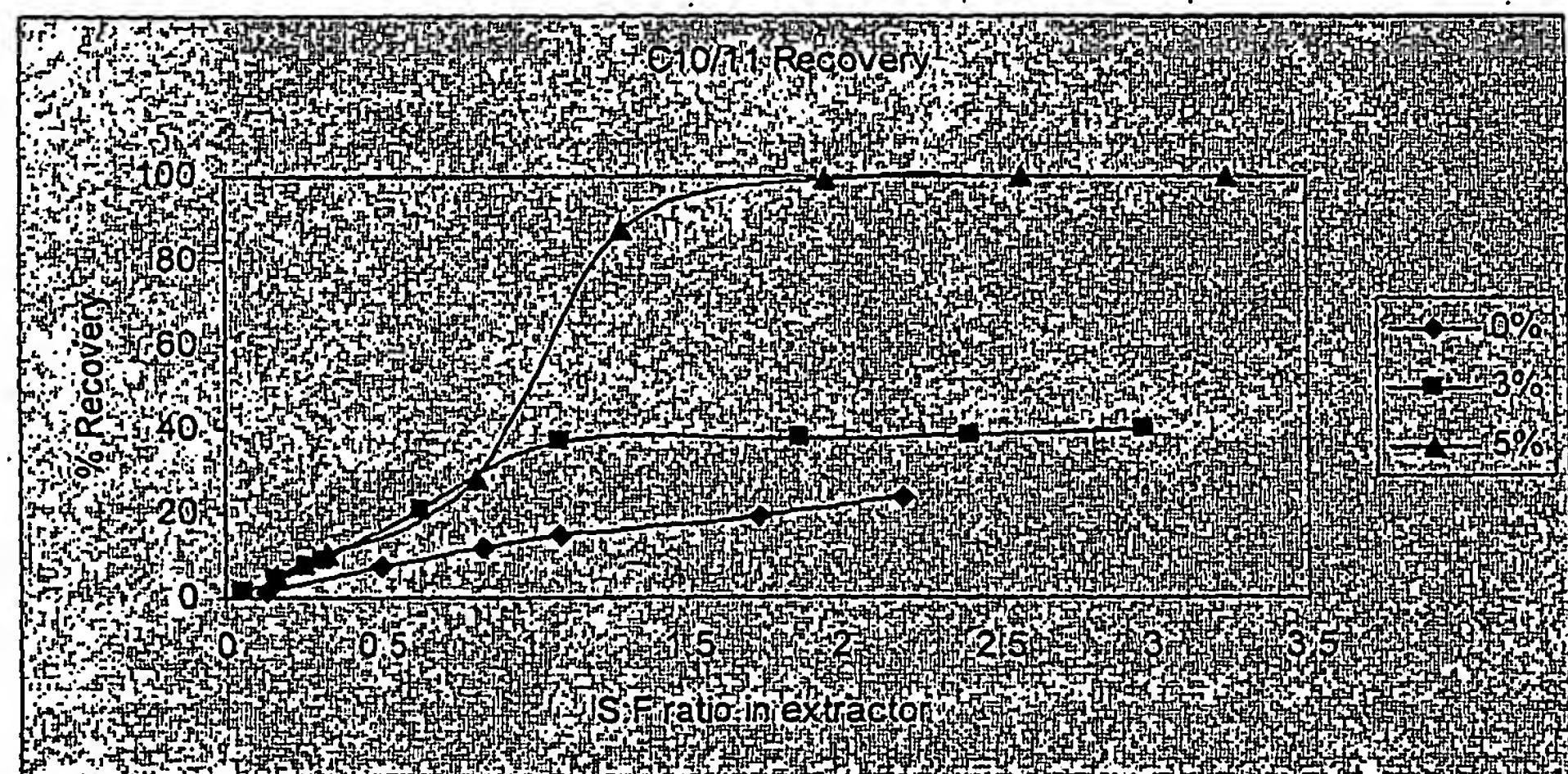
Another aspect of the invention is that, normally, a high-boiling point solvent is preferred because the solvent recovery steps after extraction require less energy than will be the case for a low-boiling point solvent. However, it has been found that a mixture of methanol and water, which is a low-boiling point solvent, need not suffer from this drawback; because it can be effective at low solvent to feed ratios (this can be lower than 1 if the required oxygenate extraction is not too severe). Furthermore, one would not expect to be able to use methanol and water as a solvent in a liquid-liquid extraction column to extract oxygenates from the abovementioned hydrocarbon condensate because a study of the different azeotropes with water that exist in the hydrocarbon condensate would lead one to expect that it would not be possible to distil water in a solvent recovery column without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case.

A further aspect of the invention is that it has been found that a water/methanol solvent, preferably with greater than 3% by weight water content in the liquid-liquid extraction column leads to better recovery of desired products in the solvent recovery column than a dry methanol solvent or a water/methanol solvent with less than 3% by weight water in the liquid-liquid extraction column. This is shown in Graph 1 below, from which it can be seen that a methanol/water solvent with 5% by weight water provides as much as 80% recovery of olefins and paraffins in the solvent recovery column. Graph 2 below shows that almost a 100% recovery of C10/C11 olefins and paraffins in the solvent recovery column is possible.

Graph 1



Graph 2



Thus, according to the invention, typically 90% of the olefins and paraffins are recovered from the liquid-liquid extraction column. The 10% of olefins and paraffins not recovered are sent to the solvent recovery column in the extract from the liquid-liquid extraction column. Up to 60% of the olefins and paraffins in the solvent recovery column are recovered in the overheads product from the solvent recovery column and recycled to the liquid-liquid extraction column. This results in an over-all recovery of olefins and paraffins of more than 90%.

With reference to the Figure, a liquid-liquid extraction process of the invention includes a liquid-liquid extraction column 20. The fractionated condensation product of a low-temperature Fischer-Tropsch reaction described above 14 is fed into the extraction column 20 at, or near, the bottom thereof. The solvent for the extraction column 20 is water and methanol. According to the invention, the water and methanol are added to the extraction column 20 separately. Methanol is added to the extraction column 20 via a methanol stream 21 at, or near, the top of the extraction column 20. Water is added to the extraction column 20 via a water stream 34 located between the hydrocarbon stream 14 and methanol stream 21. The flow of methanol and water is controlled to provide a solvent in the column with more than 5% by weight water. The solvent to feed ratio in the extraction column 20 is low, typically less than 1.5.

Raffinate 22 from the top of the extraction column 20, which includes olefins and paraffins and a small amount of solvent, enters a raffinate stripper column 23 and a hydrocarbon product stream comprising more than 90% by weight olefins and paraffins and less than 0.01% by weight oxygenates exits as a bottoms product 24. The bottoms product 24, which shows an overall recovery of over 90% of the olefins and paraffins, contains more than 20% by weight  $\alpha$ -olefins and more than 70% by weight n-paraffins. Thus, the olefin content of the hydrocarbon product (which is intended for use in the production of linear alkyl benzene) has been preserved. A solvent comprising mainly methanol (more than 90% by weight) and low concentrations of water (less than 5% by weight) and olefins/paraffins (less than 5% by weight) exits as a tops product 25 and is returned to the solvent feed stream 21. If it is desired to recover the bottoms product 24 as a vapour stream, this can be done by taking a bottoms vapour stream from the column 20. The liquid product from the column 20 will then be a very small effluent stream.

An extract 26 is drawn from the bottom of the extraction column 20 and is fed to a solvent recovery column 27. A tops product 29 from the solvent recovery column 27 comprises over 90% by weight methanol and 2% by weight olefins and paraffins. Up to 60% of the olefins and paraffins from the extract 26 are recovered to the tops product 29. The tops product is then recycled to the solvent stream 21. The oxygenate content of the tops product 29 can be as low as 50 ppm, depending on the solvent to feed ratio used in the extraction column 20. A bottoms product 28 from the solvent recovery column 27 comprises mainly water, oxygenates and olefins/paraffins. This bottoms product 28 forms two liquid phases that can be decanted in a decanter 30. The organic phase is an oxygenate, olefin and paraffin stream 31, which leaves the process as a product. The aqueous phase is a stream 32, which is recycled to the extraction column 20 via the water stream 34.

The presence of water in the extraction column 20 improves the recovery of paraffins and olefins in the raffinate stream 22. Although it is important for the water to be present in the lower section of the extraction column 20, including the point where the extract 26 is drawn from the extraction column 20, it has been found that it is not necessary for the water to be present throughout the extraction column 20. It has also been found that it is beneficial to have as little water as possible at the top of the extraction column 20 as the presence of water lowers the methanol's ability to take up oxygenates which would result in a higher solvent to feed ratio when compared to dry methanol. Thus, if as little water as possible is present in the upper section of the extraction column 20 it is beneficial in that it is possible to use a lower solvent to feed ratio than when water is added as a mixture together with methanol. Adding the water separately into the extraction column 20 between the hydrocarbon stream 14 and methanol stream 21 results in an improved paraffin and olefin recovery with better raffinate 22 purity, than if the water and methanol were added as a mixture. As mentioned above, the aqueous phase stream 32 recovered from the decanter 30 is recycled to the water stream 34 into the extractor column 20. The stream 32 may contain oxygenates and the addition of this water at a

different point to the methanol stream 21 lower down the extraction column 20 ensures that oxygenates are cleaned from the stream in the column, before they can appear in the raffinate stream 22.

With reference to Comparative Example 1 and the Example 2 of the invention below, it is evident that the process of the invention where the water and methanol are added separately leads to a lower oxygenate content in the product stream 24. Example 2 provides an oxygenate content of 0.0094% by weight in the product stream 24, while comparative Example 1 provides an oxygenate content of 0.0145% by weight in the product stream 24. Thus the product of Example 2 of the invention provides a more suitable hydrocarbon feed stream for use in the production of linear alkyl benzene. Example 2 of the invention also shows a higher overall olefin and paraffin recovery than comparative Example 1.

The invention will now be described in more detail with reference to the following non-limiting Example 2 and comparative Example 1.

#### Comparative Example 1

This example shows a comparative process where the water and methanol are introduced to the extraction column together in the solvent feed stream 21, and the stream 32 is recycled to the solvent feed stream 21. The extraction column 20 was run at a solvent to feed ratio of 1.25 and a temperature of 50°C. The overall olefin/paraffin recovery in the stream 24 was 89.9%, with an  $\alpha$ -olefin concentration of 21.6% by weight, n-paraffin concentration of 72.2% by weight and 0.3% by weight branched hydrocarbons and 5.9% by mass internal olefins.

Extraction column 20

Stream	14		21		22		26	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	3000	100	3750	100	2530	100	4220
Total C10-C13 P/O	92.7	2779.7	2.16	81.0	99.1	2507.9	6.20	261.7
Total Oxygenates	7.3	217.7	0.000	0.000	0.0144	0.365	5.78	243.7
Lights and Heavies	0.057	1.7	0.004	0.144	0.0104	0.263	0.00480	0.202
Water	0.031	0.934	6.01	225.6	0.0073	0.184	5.74	242.4
Methanol	0.000	0.000	91.7	3443.3	0.842	21.31	82.3	3472.0

Raffinate Stripper column 23

Stream	22		25		24	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	2530	100	30	100	2500
Total C10-C13 P/O	99.1	2507.9	2.63	0.793	99.97	2499.4
Total Oxygenates	0.0144	0.365	0.00163	0.000491	0.0145	0.363
Lights and Heavies	0.0104	0.263	0.0887	0.0267	0.00808	0.202
Water	0.0073	0.184	1.52	0.456	0.00115	0.0288
Methanol	0.842	21.31	95.4	28.7	0.000	0.000

Solvent Recovery column 27

Stream	26		29		28	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	4220	100	3584	100	636
Total C10-C13 P/O	6.20	261.7	2.37	85.1	27.6	175.8
Total Oxygenates	5.78	243.7	0.00140	0.0503	42.0	267.0
Lights and Heavies	0.00480	0.202	0.00747	0.268	0.00279	0.0177
Water	5.74	242.4	1.30	46.8	29.3	186.6
Methanol	82.3	3472.0	96.2	3451.9	1.04	6.63

Example2

This example shows a process according to the invention where the methanol and water are introduced to the extraction column in separate streams 21 and 34 respectively. The extraction column 20 was run at a solvent to feed ratio of 1.2 and a temperature of 50°C. The overall olefin/paraffin recovery in the stream 24 was 92.3%, with an α-olefin concentration of 21.6% by weight, n-paraffin concentration of 72.2% by weight and 0.3% by weight branched hydrocarbons and 5.9% by weight internal olefins.

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## Extraction column 20

Stream	14		34		21		22		26	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	3000	100	179	100	3334	100	2599	100	3914
Total C10-C13 P/O	92.6	2778.8	0.000	0.000	2.11	70.3	99.0	2572.1	7.89	308.8
Total Oxygenates	7.34	220.3	0.000	0.000	0.000	0.000	0.00937	0.244	6.00	234.9
Lights and Heavies	0.0156	0.470	0.000	0.000	0.009	0.298	0.00292	0.0758	0.00813	0.318
Water	0.0164	0.492	94.9	169.9	0.29	9.7	0.00270	0.0702	4.89	191.4
Methanol	0.000	0.000	5.07	9.07	97.6	3253.7	1.02	26.5	81.2	3178.6

## Raffinate Stripper column 23

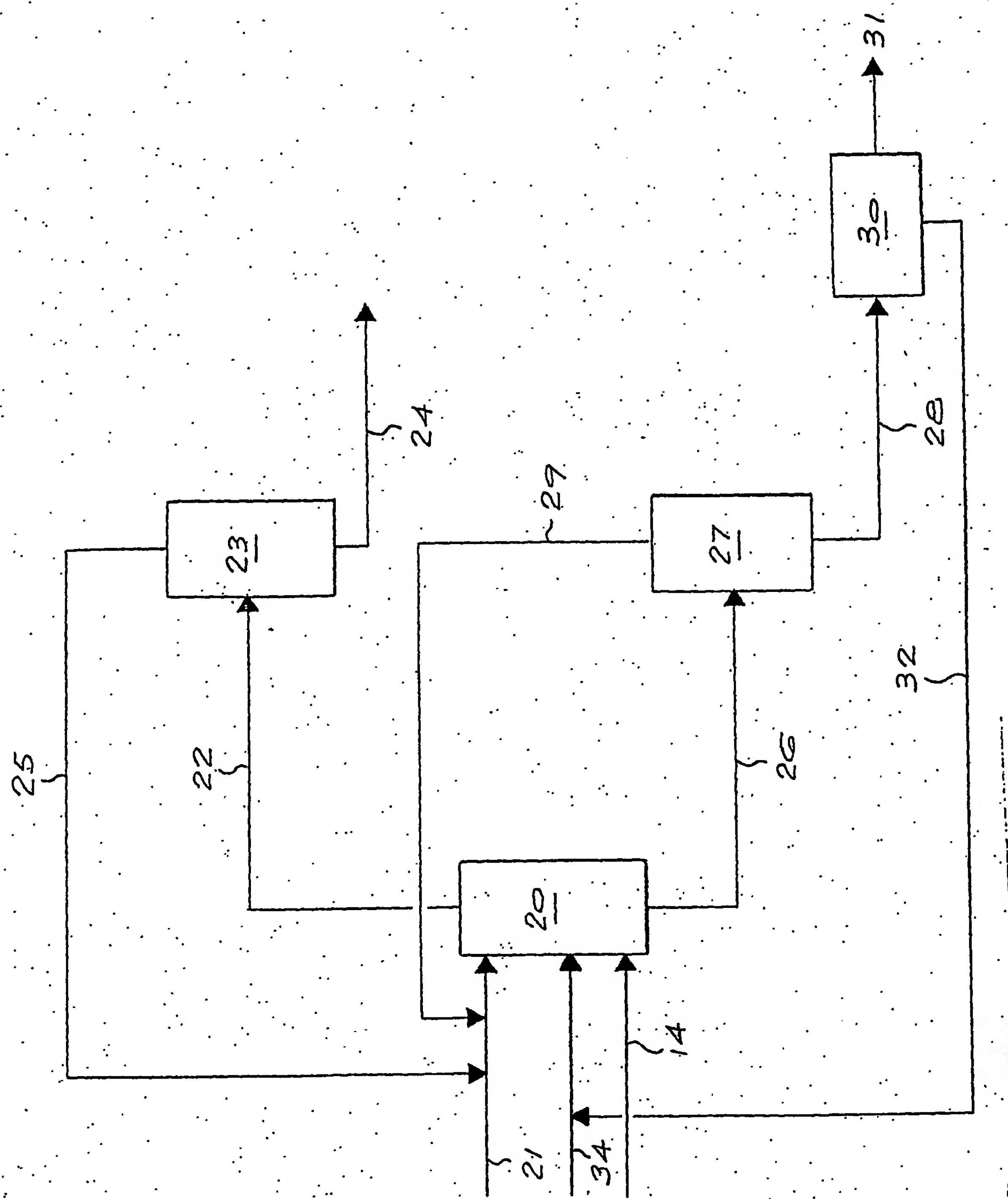
Stream	22		25		24	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	2599	100	33	100	2566
Total C10-C13 P/O	99.0	2572.1	2.01	0.663	99.98	2565.73
Total Oxygenates	0.00937	0.244	0.00647	0.00213	0.0094	0.24122
Lights and Heavies	0.00292	0.0758	0.0708	0.0234	0.00048	0.01258
Water	0.00270	0.0702	0.210	0.0693	0.00050	0.01280
Methanol	1.02	26.5	97.7	32.2	0.000	0.0

## Solvent Recovery column 27

Stream	26		29		28	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	3914	100	3171	100	743
Total C10-C13 P/O	7.89	308.8	2.01	63.8	34.8	258.4
Total Oxygenates	6.00	234.9	0.00335	0.1	32.9	244.8
Lights and Heavies	0.00813	0.318	0.00237	0.075	0.00869	0.0646
Water	4.89	191.4	0.22	7.0	28.7	213.6
Methanol	81.2	3178.6	97.8	3100.0	3.51	26.09

Dated this 21<sup>st</sup> day of August 2003


Spoor & Fisher  
Applicant's Patent Attorneys



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